

## Proton-Coupled Electron Transfer Between Metal-Bound Ligands and Organic Radicals

James M. Mayer, Justine P. Roth, Jeffrey C. Yoder  
Department of Chemistry, University of Washington  
Campus Box 351700, Seattle, WA 98195-1700

Transition metal complexes that have an affinity for an electron and a proton can abstract a hydrogen atom — a proton and an electron — from organic substrates. For instance, the deprotonated iron(III) tris(bi-imidazoline) complex  $[\text{Fe}(\text{Hbim})(\text{H}_2\text{bim})_2]^{2+}$  (**1**) reacts with dihydroanthracene to give anthracene and the iron(II) complex  $[\text{Fe}(\text{H}_2\text{bim})_3]^{2+}$  (**2**; see equation below). Mechanistic studies indicate that this reaction proceeds by one-step proton-coupled electron transfer (hydrogen atom transfer), rather than by stepwise pathways of electron transfer followed by proton transfer or vice versa. The reaction occurs because of the fairly high affinity of **1** for a hydrogen atom (the N–H bond strength in **2**). This was determined to be  $76 \pm 2 \text{ kcal mol}^{-1}$  using a thermochemical cycle involving the redox potential and  $\text{pK}_a$  values.

The rate constant for iron abstracting  $\text{H}\cdot$  from dihydroanthracene correlates with related reactions of oxygen radicals, based on the differences in bond strengths. Such correlations of rate with bond strength are typical for organic hydrogen atom transfer reactions (Bell-Evans-Polanyi relation), but have not been widely applied to proton-coupled electron transfer.

The Marcus cross relation,  $k_{12} = (k_{11}k_{22}K_{\text{eq}})^{1/2}$ , is a related type of correlation. To probe whether this relation will apply to proton-coupled electron transfer / hydrogen atom transfer, we have measured the rate of hydrogen atom self-exchange between **1** and **2**, by proton NMR line broadening. It is a concerted rather than a stepwise transfer of proton and electron. Related iron and cobalt complexes are also under study.

Reactions of these various compounds with phenols, phenoxyl radicals, hydroxylamines, and nitroxide radicals have been examined. For instance, **2** is oxidized by the stable 2,4,6-tri(t-butyl)phenoxyl radical to yield the phenol and **1** (see equation below). For many of these substrates hydrogen atom-self exchange rates are known. These values, the self exchange and cross rates we have measured, and our electrochemical and  $\text{pK}_a$  measurements enable a clear test of the Marcus cross relation. Preliminary results suggest that the cross relation will be a very valuable starting point for this class of reactions. The implication of these results will be discussed.

